THE CONDENSATION OF FORMALDEHYDE WITH UREA AND ITS DERIVATIVES

STRUCTURE OF THE UREA-FORMALDEHYDE POLYMER

BY

HENRY YUSKA

B.S., College of the City of New York, 1935
M.S., Brooklyn Polytechnic Institute, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY IN THE GRADUATE SCHOOL OF THE UNIVERSITY OF ILLINOIS, 1942

URBANA, ILLINOIS
1942

THE CONDENSATION OF FORMALDEHYDE WITH UREA AND ITS DERIVATIVES

STRUCTURE OF THE UREA-FORMALDEHYDE POLYMER

BY

HENRY YUSKA

B.S., College of the City of New York, 1935
M.S., Brooklyn Polytechnic Institute, 1939

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1942

URBANA, ILLINOIS
1942

ACKNOWLEDGMENT

The author wishes to express his deepest gratitude and appreciation to Professor Carl S. Marvel for suggesting these problems and for his invaluable advice and encouragement during the course of the investigation. He is also indebted to the University of Illinois for the grant of a Fellowship for the academic year 1941-1942.

THE CONDENSATION OF FORMALDEHYDE WITH UREA AND ITS DERIVATIVES

STRUCTURE OF THE UREA-FORMALDEHYDE POLYMER

Introduction

The purpose of this investigation was to prepare condensation products of substituted ureas with formaldehyde, and to compare these products with those obtained in the reaction of urea and formaldehyde. Whereas urea is very reactive toward formaldehyde and quickly forms complex mixtures of high molecular weight; the substituted ureas, which have fewer reactive hydrogen atoms, may be expected to form simpler products more amenable to study. The mechanism of the urea-formaldehyde reaction and the structure of the polymer may thus be classified.

Results and Conclusions

The methyl[1] and butyl ethers of α,α-dimethyl-β-monomethylolurea were prepared; however it was found that they did not form polymers when treated with either acids or alkalies. In acid solution these compounds were transformed into α,α'-methylenebis [β,β-dimethylurea], and in alkaline solution into α,α-dimethylurea.

Other substituted ureas were then condensed with formaldehyde to determine whether they too yielded lower condensation products, and not polymers. It had been previously[2] assumed that soluble, linear polymers were formed. The substituted ureas studied were methylurea, ethylurea, *sec*-butylurea, phenylurea, α,β-diphenylurea, α-phenyl-β-methylurea, α-phenyl-β-*n*-butylurea, acetylurea, α,β-diacetylurea, α-acetyl-β-methylurea and α,β- di-*n*-butylurea. In no case were polymers obtained. In each case the condensation products of the reaction in alkaline and acid solution were isolated and identified. In alkaline solution the condensation products were

the α-methylol-methylenebis substituted ureas (e.g. phenylurea gave α-methylol-α,α'methylenebis [β-phenylurea]) and in acid solution the products were the methylenebis substituted ureas (e.g. α,α'-methylenebis [β-phenylurea]). When the substituent of the substituted urea was a phenyl or acetyl group, the remaining hydrogen of the substituted nitrogen atom did not react with formaldehyde. When the substituent was a methyl or butyl group, the reaction was hindered. Thus α,β-diphenylurea and α,β-diacetylurea gave no condensation products in either alkaline or acid solution. α-Phenyl-β-methylurea and α-acetyl-β-methylurea did not react in alkaline solution but did give rather unstable products in acid solution, respectively α,α'-methylenebis [α-methyl-β-phenylurea] and α,α'-methylenebis [α-methyl-β-acetylurea].

The mechanism of the reaction between substituted ureas and formaldehyde has been found to involve a step-wise condensation process. This has been proved by isolating the products formed in each step of the condensation. For phenylurea these steps were α-methylol-α,α'-methylenebis [β-phenylurea] and α,α'-methylenebis [β-phenylurea].

A simple, qualitative test to distinguish between methylol and methylenebis substituted ureas has been developed, involving the use of phenol in concentrated sulfuric acid.

The data obtained with substituted ureas may be used to interpret the urea-formaldehyde[3] reaction since both reactions depend upon the same factors and yield analogous products. The conclusion may therefore be drawn that the urea-formaldehyde reaction is (a) a step-wise condensation process and not a vinyl type polymerization (b) that methylene groups link the urea radicals in the final product.

It is proposed that the urea-formaldehyde polymers be divided into two classes; (a) those formed in strong acid solution, at low temperatures, without the use of excessive amounts of formaldehyde (b) those formed at high temperatures in neutral or slightly acidic solution, in the presence of large excesses of formaldehyde. The first type (the so-called methyene ureas A and B[4]) closely resemble the methylenebis substituted ureas in their insolubility, high-melting characteristics and

stability. Polymers of the second type are soluble, unstable, viscous liquids containing many methylol groups; and possibly of the "uron" ring type of Kadowaki.[1]

Bibliography

1. Kadowaki, Bull. Chem. Soc. Japan **11**, 248 (1936).
2. Glass, Thesis, Doctor of Philosophy, University of Illinois, 1939.
3. Einhorn, Ann. **361**, 113 (1908).
4. Walter, Trans. Faraday Soc. **32**, 377 (1936).

VITA

The author was born in Brooklyn, New York on November 7, 1914. He attended the elementary schools and Boys High School of that city. He continued his education at the City College of New York and received the degree of Bachelor of Science in June, 1935. From 1936 to 1939 he continued his education in chemistry on a part-time basis at the Brooklyn Polytechnic Institute, graduating in June, 1939 with the degree of Master of Science in Chemistry. In the fall of 1939 he entered the Graduate School at the University of Illinois. He was an Assistant in Chemistry from February to June, 1941. For the academic year 1941-1942 he held a University Fellowship.

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549818_0305